Excavation and Investigation of a Permeable Reactive Barrier in Cañon City, Colorado

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Abstract

Permeable reactive barriers (PRBs) are engineered zones of reactive materials placed in an aquifer such that contaminants are removed from the ground water as it flows through the reactive matrix. PRBs employing granular zero-valent iron (ZVI) as the reactive media have been used since the early 1990s to treat trichloroethene (TCE) and other chlorinated solvents. Since about 1998, PRBs have also been used for the removal of radionuclides and metals. Many investigations of PRBs, including bench-scale and column tests, have shown that ZVI corrosion causes mineral precipitation within the PRB that impedes the performance and may significantly impact the design life and, therefore, the cost effectiveness. Research being conducted by the U.S. Department of Energy (DOE) and the U.S. Environmental Protection Agency (EPA) is evaluating the performance of PRBs for long-term application at sites where radionuclides are present. Initial findings indicate that clogging (porosity loss) may be a significant issue at some sites.

In June 2000, construction was completed on a PRB at a uranium-ore milling site operated by Cotter Corporation in Cañon City, Colorado. This PRB uses ZVI as the reactive media to mitigate molybdenum and uranium contamination. The PRB, proposed in a 1999 CERCLA Record of Decision, was installed with the purpose of minimizing the flow of contaminated ground water into the Lincoln Park subdivision that is located approximately 1 mile downgradient from the mill. Within 2 years of construction, monitoring results indicated significant mounding at the upgradient surface of the PRB and contaminant bypass of the barrier. EPA, DOE, Colorado Department of Public Health and Environment (CDPHE), and Cotter Corporation collectively decided to excavate the wall to determine what mechanisms had caused failure of the PRB and to investigate whether the PRB could be rejuvenated.

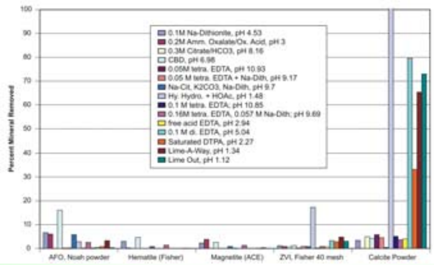
Following the excavation and tests of the reactive media, recommendations for improving the efficiency of the Cotter PRB were developed. They include

(1) Reconfiguring the PRB to allow accessibility so that the ZVI can either be maintained or changed out when necessary,

(2) Flushing the existing system with weak acids to restore hydraulic conductivity, and/or

(3) Installing a pretreatment zone consisting of coarse gravel mixed with ZVI that can extend the performance life of the PRB.

EPA and DOE believe the lessons learned will help in the future design of PRBs so that they can be more easily monitored and maintained.



Results of batch tests (orbital shaking for 2 hours).

Rejuvenation

Bench-scale tests were conducted to evaluate the potential for rejuvenation of ZVI PRBs using chemical solvent flushing

- Tested EDTA, tetrasodium EDTA, disodium EDTA, DPTA, ammonium oxalate, sodium dithionite, sodium citrate, hydroxlyamine hydrochloride, Lime Away, and Lime Out; some tests conducted with combinations
- Some tests included bicarbonate or carbonate as a pH buffer
- Tested on monomineralic samples of typical corrosion products
- Favorable substances dissolved calcite but not ZVI and have low toxicity
- Ability to dissolve amorphous ferric oxyhydroxide (AFO), magnetite, and hematite also considered favorable
- Best results with tetrasodium EDTA and disodium EDTA

Conducted column tests

- EDTA removed all the calcite deposited during ZVI corrosion and some of the calcite initially present in the column fill material
- Some ZVI also dissolved by EDTA but insignificant change in Fe inventory

Permeable Reactive Barrier

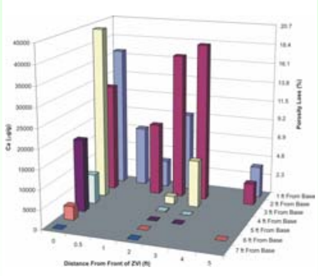
In June 2000, construction was completed on a PRB at a uranium-ore milling site operated by Cotter Corporation near Cañon City, Colorado

- 30-ft-wide reactive zone contains 80 tons of Peerless –8 +50 mesh ZVI
- 370 ft of Hypalon funnel walls
- Molybdenum (Mo) main contaminant with mean influent concentration of 4.8 mg/L
- PRB functioned well for about 1 year, then Mo concentrations increased in effluent
- Mo concentrations were higher in effluent than in influent by January 2003
- Ground water mounded upgradient and bypassed the PRB
- ZVI decreased in hydraulic conductivity

In October 2004, west end of PRB exposed in an excavation to provide direct observation of the ZVI

- ZVI had become cemented
- Solid-phase Mo to 4,050 µg/g; highest values within 0.5 ft of upgradient front of PRB
- Solid-phase calcium (Ca) to 44,200 µg/g; high throughout most of the ZVI
- Microscopy results indicate that calcium carbonate occurs as crystalline blades
- Crystals often are grown into pores and occlude some of the porosity
- Iron oxides prevalent and further decrease porosity
- Late-stage sulfides overlie and intermix with other corrosion products

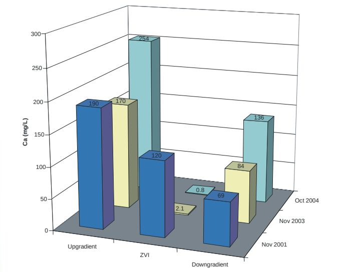
Excavation showing rigid wall of ZVI.



Solid-phase Ca distribution.

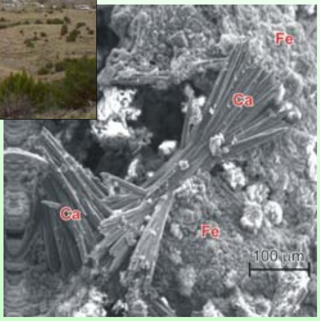
View of uranium mill.

Installation of PRB.

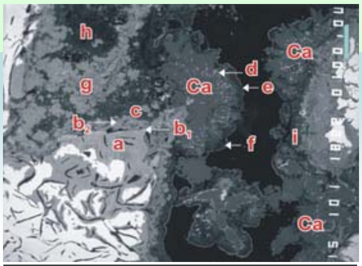


Dissolved concentrations of Ca showing bypass.

View of Lincoln Park area from millsite.



Scanning electron photomicrograph showing crystals of calcium carbonate (Ca) coating iron oxide (Fe).



Spot	Weight, %						Description
	Ca	U	Mo	Fe	S	Si	
a			0.48	64	0.6	4.2	Probably FeOx (hydrate)
b_1	1.1	1.0	6.4	52	6	4.8	Slightly Lighter Edge
b_2	1.4	0.27	6.5	58	6	3.4	
c	0.14	<.05	1.1	32	13	1.0	
d	1.5	0.07	0.43	56	29	1.6	White Spots
e	0.16	0.07	0.35	41	8	2.8	Darker zone
f			0.12	50	12	0.6	Lighter Rim
g	0.79	0.07	6.3	58	8	1.7	Lighter Material
h	0.1		1.0	27	12	0.8	
i	0.2	0.12	0.72	33	14	1.0	
Ca							Calcium Carbonate

Electron microprobe photomicrograph of sample near the front of the PRB. Blue bar is 100 mm.

Acknowledgments

The U.S. Environmental Protection Agency (EPA) provided funding for this project. The project was conducted through a collaboration among EPA, Colorado Department of Public Health and Environment (Phil Stoffey and Edgar Ethington), U.S. Department of Energy (Art Kleinrath), and Cotter Corporation (Preston Niesen). Work was performed under DOE contract number DE–AC01–02GJ79491 for the U.S. Department of Energy, Grand Junction, Colorado.

Colorado Department of Public Health and Environment

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2005
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